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Analysis of reasons for decline of bioleaching efficiency of spent Zn–Mn batteries at high pulp densities and exploration measure for improving performance

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ABSTRACT

The reasons for decline of bioleaching efficiency of Zn and Mn from spent batteries at high pulp densities were analyzed; the measures for improving bioleaching efficiency were investigated. The results showed that extraction efficiency of Zn dropped from 100% at 1% of pulp density to 29.9% at 8% of pulp density, with Mn from 94% to only 2.5%. It was almost the linear reduction of the activity of the sulfur-oxidizing bacteria with increase of pulp density that witnessed declined bioleaching efficiency of Zn; it was the complete inactivation of the iron-oxidizing bacteria at 2% of pulp density or higher that witnessed declined bioleaching dose of Mn. By means of reducing initial pH value of leaching media, increasing concentration of energy matters and exogenous acid adjustment of media during bioleaching, the maximum extraction efficiency of almost 100% for Zn and 89% for Mn at 4% of pulp density was attained, respectively.

1. Introduction

The production and consumption of batteries have been increasing in the last decades (De Souza et al., 2001). Thus, a great number of spent batteries were produced worldwide, which caused a serious concern due to their toxicity, abundance and permanence in the environment (Li and Xi, 2005). Disposal of spent batteries represented an increasing environmental problem facing the stricter regulations to control the resulting metals pollution (Ruffino et al., 2011). On the other hand, the great contrast between the growing shortage of natural resources and the high content of valuable metals such as Co, Ni, Li, Mn, Zn, Cu, Al, Pb and so on in the spent batteries (Senanayake et al., 2010; Vassura et al., 2009), endowed recovery of these metals from the spent batteries as secondary sources with an attractive issue and prior status in recent years (Kim et al., 2009). Therefore, recycling of the waste batteries was an important subject not only from the viewpoint of treatment of hazardous waste but also with respect to recovery of valuable metals (Huang et al., 2010).

The portable batteries included mainly alkaline and zinc–carbon batteries as primary batteries as well as Ni–Cd, Ni–MH and Li–ion batteries as secondary batteries. Various spent batteries drew concentrated studies for purpose of recovering the valuable and precious metals using different processes (Freitas et al., 2010; Ferella et al., 2008; Huang et al., 2010; Li et al., 2009). Among the portable batteries, the primary Zn–Mn batteries occupied about 90% of the total annual sales because of very low price and they run out rapidly and thrown away, representing a major environmental and health threat (Kierkegaard, 2007). As a result, recycling of Zn–Mn batteries carried more attentions and was reviewed in detail recently (Sayilgan et al., 2009). As the most widely used hydrometallurgical process, acid leaching was frequently used to release both Zn and Mn from the spent Zn–Mn batteries in the presence of strong acid solution such as H_2SO_4, HCl, HNO_3 and so on (Sayilgan et al., 2009).

In most cases, acid leaching witnessed nearly 100% of Zn extraction from the spent batteries, but Mn dissolution was rather poor due to insoluble MnO_2; moreover, the heavy consumption of various strong acids endowed the leaching process with high cost, strict requirements of equipment and potentially safe risk (Sayilgan et al., 2009). The reductive acidic leaching could greatly improve extraction yield of Mn by adding inorganic reductants such as H_2O_2 and SO_2 or organic ones such as glucose, sucrose, lactose, oxalic acid, citric acid, tartaric acid, formic acid and triethanolamine, but higher safety risk and greater operation cost occurred (Sayilgan et al., 2009). So, developing the environmentally-friendly and cost-effective recycling methods for the spent Zn–Mn batteries should be encouraged (Sayilgan et al., 2009).

At present, biohydrometallurgical processes (bioleaching-tech) have been gradually replacing hydrometallurgical ones due to their higher efficiency, lower cost and few industrial requirements (Rossi, 1990). Bioleaching was characterized by efficient release of metals from solid phase into aqueous solution under the mild

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conditions of room temperature and pressure by contact and/or non-contact mechanisms in the presence of acidophilic sulfur-oxidizing and/or iron-oxidizing bacteria (Rohwerder et al., 2003). For a long time, bioleaching was widely used for low-grade ore metallurgy (Qiu et al., 2011), removal of toxic heavy metals from sludge (Wang et al., 2010) and recovery of precious metals from waste printed circuit boards (Zhu et al., 2011). In recent years, utilization of bioleaching for recovery of valuable metals Co, Li, Ni, Cd from spent nickel–cadmium batteries and lithium ion batteries has attained growing attentions (Cerruti et al., 1998; Mishra et al., 2008a; Xin et al., 2009; Zhao et al., 2008). However, there were few reports about bioleaching of spent Zn–Mn batteries for recovery of valuable metals Zn and Mn (Xin et al., 2012).

For practical application of bioleaching, the pulp density, i.e. the ratio of the solid material (W) to bioleaching media (V), was a very important parameter which greatly affected the operational cost and subsequent separation. Taking the alteration of pulp density from 1% to 2% for example, 1% meant that one gram of solid material needed 100 ml of bioleaching media; whereas with 2% only 50 ml of media was required. The increase in pulp density from 1% to 2% resulted in decrease of bioleaching media by 50%, bringing a sharp decline in operational cost; meanwhile, the extraction concentration of metals rose by 100% if the bioleaching efficiency of metals kept unchanged, being favorable to the subsequent separation of metals from aqueous solution. However, all the previous studies with respect to the bioleaching of spent batteries in batch culture were based on pulp density of 1% or lower due to very high content of metals and alkaline matter in the waste batteries which were toxic to the bioleaching bacteria (Cerruti et al., 1998; Mishra et al., 2008a; Xin et al., 2012, 2009). So far, the bioleaching performance of spent batteries, reasons analysis for decline of bioleaching efficiency and the countermeasures exploration for improving the bioleaching yields at pulp density of 2% or higher were not available.

In previous paper, the bioleaching property and mechanism of spent Zn–Mn batteries at pulp density of 1% were studied in detail (Xin et al., 2012). In the present studies, the bioleaching performance of spent Zn–Mn batteries at pulp density of 2% or higher was investigated. The objects of the current works were (I) to compare the bioleaching dynamics of Zn and Mn from the spent batteries under different pulp densities ranging from 1% to 8%; (II) to analyze the reasons for decrease of bioleaching efficiency at high pulp densities; and (III) to propose the measures for improving the bioleaching efficiency at high pulp density of 4%.

2. Methods

2.1. Batteries dismantling and powder preparation

Spent alkaline and zinc–carbon batteries were artificially dismantled as described previously (Xin et al., 2012). The powders, equivalent to ca. 40–64% of the total weights of dismantling batteries (Sayilgan et al., 2010), were mixed, washed, dried, ground by milling and sieved to obtain a mesh size of less than 200 μm (Mishra et al., 2008a). The resulting powder was used for bioleaching experiments.

The resulting powder was digested by HF–HNO_3–HCl digestion method (USEPA, 1995). The content of Zn and Mn was 280 and 350 g/kg respectively by atomic absorption spectrophotometer, higher than that of the previous (Xin et al., 2012).

2.2. Microorganisms and media

The Alicyclobacillus sp. as sulfur-oxidizing bacteria and the Sulfobacillus sp. as iron-oxidizing bacteria were utilized for bioleaching the spent Zn–Mn batteries in the form of mixed culture. Elemental sulfur and $FeSO_4$ were used as energy substrates to grow the Alicyclobacillus sp. and Sulfobacillus sp. respectively, for the sake of regular maintain and inoculum (Xin et al., 2012). The detailed procedures and methods about screen, culture, maintain, inoculum and identification of the sulfur-oxidizing and iron-oxidizing bacteria were described in the previous paper (Xin et al., 2009, 2011). Prior to use as inoculum, both of the acidithiobacillus were adapted by addition of $ZnSO_4$ and $MnSO_4$ ranging from 0.5 to 5.0 g/l over a period of 30 days according to the methods described by Cerruti et al. (1998). The bioleaching media were prepared by adding mixed energy matters of elemental sulfur and pyrite into the basic medium containing $(NH_4)_2SO_4$, 2.0 g; KH_2PO_4, 1.0 g; $MgSO_4{\cdot}7H_2O$, 1.0 g; $CaCl_2$, 0.25 g; $FeSO_4{\cdot}7H_2O$, 0.18 g; distilled water, 1000 ml; natural pH 5.5.

2.3. Extraction behavior of Zn and Mn from the spent Zn–Mn batteries by bioleaching under different pulp densities

The bioleaching media containing a mixed energy source of both 2.0 g/l elemental sulfur and 2.0 g/l pyrite was prepared and placed into 250 ml flasks at a portion of 100 ml per flask. Both of the acidithiobacillus at 5% (v/v) for each as mixed culture were inoculated respectively into the flasks containing bioleaching media and incubated in a shaker at 30 °C at 120 rpm. After 12 days culture, when the pH value of bioleaching media decreased from about 4.0 to 1.1 ± 0.1, different amount of batteries powder was added into the flasks containing media to the final concentration of 1%, 2%, 4% and 8% (w/v), respectively. The batteries materials-contained flasks were continuously incubated in the shaker to carry out bioleaching. In the course of bioleaching, the released concentrations of Zn and Mn were measured; the Oxidation–Reduction Potential (ORP) value and the pH value of the solutions were monitored. The sterile controls were performed in the absence of bacteria using filter-sterilized medium at initial pH of 5.5 synchronized with the above-mentioned flasks. All the experiments, including the sterile controls, were carried out in triplicates.

2.4. Reasons analysis for decrease of bioleaching efficiency at high pulp densities

2.4.1. Cell number monitoring of the mixed culture under different pulp densities

During bioleaching, the cell number of the mixed culture from different pulp densities was counted using a microscope after the samples were treated by ultrasonic to release the adherent bacteria. The cell number reflected the growth of the mixed culture which affected the bioleaching efficiency.

2.4.2. Activity test of each acidithiobacillus from different pulp density systems

At the end of bioleaching experiments, the flasks were treated by ultrasonic for 10 min to release the adherent bacteria into aqueous solution. After 30 min of standing, 10 ml of the upper layer of suspension in the flasks was withdrawn, centrifuged (10000 rpm, 10 min), washed three times with sterile normal saline and suspended again with the same normal saline to a final volume of 10 ml for removing the dissolved Zn and Mn as well as the residual batteries. The resulting suspensions of mixed culture from pulp density of 1%, 4% and 8% were inoculated respectively into 100 ml of fresh bioleaching media containing either 2.0 g/l elemental sulfur or 2.0 g/l pyrite. The inoculated leaching media were incubated in a shaker at 30 °C at 120 rpm. With pyrite the Oxidation–Reduction Potential (ORP) value was measured to explore the activity of iron-oxidizing bacteria of the mixed culture from different pulp densities; with elemental sulfur the pH value of the solutions was monitored to reflect the activity of the sulfur-oxidizing bacteria of the mixed culture. The sterile controls were

performed in the absence of bacteria using filter-sterilized medium at initial pH of 5.5 synchronized with the above-mentioned flasks. All the experiments were carried out in triplicates.

2.4.3. Tolerance test of the mixed culture to high concentration of Zn^{2+} and Mn^{2+}

The bioleaching media containing a mixed energy source of both 2.0 g/l elemental sulfur and 2.0 g/l pyrite was added both Zn^{2+} mother liquor in the form of $ZnSO_4$ and Mn^{2+} mother liquor in the form of $MnSO_4$ to a final concentration of 10 g/l for each ion, followed by transfer into 250 ml flasks at a portion of 100 ml per flask. Both of the adapted acidithiobacillus at 5% (v/v) for each as mixed culture were inoculated respectively into the flasks containing bioleaching media and incubated in a shaker at 30 °C at 120 rpm. The Oxidation–eduction Potential (ORP) value and the pH value of the solutions were monitored reflecting the tolerance of the mixed culture to high concentration of released metals. The control experiments were performed in the absence of both Zn^{2+} and Mn^{2+} synchronized with the above-mentioned flasks. All the experiments were carried out in triplicates.

2.5. Improving bioleaching performance of the spent batteries at pulp density of 4% by reducing the initial pH value of bioleaching media

The bioleaching media containing 2.0 g/l elemental sulfur and 2.0 g/l pyrite as mixed energy matters were prepared, inoculated and incubated as described above. After 12 days of culture, the pH value of bioleaching media decreased from about 4.0 to 1.0–1.2. The initial pH value of 1.0, 2.0 and 3.0 was obtained by precisely adjusting the 12 day-cultured bioleaching media with 0.5 mol/l H_2SO_4 or NaOH. At that moment, the spent batteries powder was added into the bioleaching media with varied pH value to final concentration of 4% (w/v), respectively. The batteries materials-contained flasks were continuously incubated in the shaker to perform bioleaching. During bioleaching, the released concentrations of Zn and Mn were measured; the Oxidation–Reduction Potential (ORP) value and the pH value of the solutions were monitored. The sterile controls were run as described above. All the experiments, including sterile controls, were carried out in triplicates.

2.6. Improving bioleaching performance of the spent batteries at pulp density of 4% by increasing concentration of energy matters of bioleaching media

The bioleaching media containing different doses of elemental sulfur and pyrite as the mixed energy substrates, i.e. 2.0 + 2.0 g/l, 4.0 + 4.0 g/l, 8.0 + 8.0 g/l, were prepared, inoculated and incubated as described above. After 10 days of culture, the pH value of bioleaching media with 8.0 g/l sulfur + 8.0 g/l pyrite first decreased from about 4.0 to 1.0–1.2. At that moment, the initial pH value of bioleaching media with different doses of mixed energy matters was adjusted precisely to 1.0 with 0.5 mol/l H_2SO_4 or NaOH, followed by adding the batteries materials to final concentration of 4% (w/v). The batteries materials-contained flasks were continuously incubated in the shaker to perform bioleaching. During bioleaching, the released concentrations of Zn and Mn were measured, the Oxidation–Reduction Potential (ORP) value and the pH value of the solutions were monitored. The sterile controls were run as described above. All the experiments, including sterile controls, were carried out in triplicates.

2.7. Improving bioleaching performance of the spent batteries at pulp density of 4% by exogenous-acid adjustment of media during bioleaching

The bioleaching media containing mixed energy substrates of 8.0 g/l elemental sulfur + 8.0 g/l pyrite were prepared, inoculated and incubated as described above. After 10 days of culture, the pH value of bioleaching media decreased from about 4.0 to 1.0–1.2. At that moment, the initial pH value of bioleaching media was adjusted precisely to 1.0 with 0.5 mol/l H_2SO_4 if needed, followed by adding batteries materials to final concentration of 4% (w/v). The batteries materials-contained flasks were continuously incubated in the shaker to perform bioleaching. During bioleaching, the pH value of media was periodically adjusted to 2.0 with 0.5 mol/l H_2SO_4 for fitting the growth of both acidithiobacillus leaching bacteria. Before each adjustment of pH with exogenous acid, the extracted contents of Zn and Mn were measured; the Oxidation–Reduction Potential (ORP) value and the pH value of the solutions were monitored. Because the addition of exogenous H_2SO_4 for acidic adjustment also inevitably resulted in release of Zn and Mn, the actual extraction concentrations of Zn and Mn by bioleaching were the difference value of the above-mentioned measured value subtracting the released dose of Zn and Mn in controls flasks without both energy matters and bioleaching bacteria, into which only the same amount of exogenous H_2SO_4 was added synchronized with the bioleaching flasks. All the experiments were carried out in triplicates.

2.8. Apparatuses and conditions

The pH value of bioleaching media was determined using a precise pH meter, the ORP value was determined by portable ORP meter; the released dose of Zn and Mn was determined by atomic absorption spectrophotometer (361MC, Shanghai Precision Scientific Instrument Co., Ltd., China). Morphology change of batteries residues after bioleaching was analyzed by scanning electron microscope (SEM, Hitachi S-4800, Japan) at an accelerating voltage of 20 kV. Micro-area chemical analysis was performed by energy dispersive X-ray analysis (EDX, Oxford) operating at 20.0 keV. Structure change analysis was performed by X-ray diffractometer (XRD, Shimdzu) with Cu Ka radiation (k = 1.5418).

3. Results and discussion

3.1. Extraction behavior of Zn and Mn from the spent Zn–Mn batteries by bioleaching under different pulp densities

The released concentrations of both Zn and Mn as well as the variation of both pH value and ORP value under different pulp densities as a function of bioleaching time were illustrated in Fig.1. In the spent Zn–Mn batteries, Zn existed in the form of ZnO which was readily soluble in acidic solution; whilst Mn existed in the form of Mn_2O_3 or Mn_3O_4 containing soluble MnO and insoluble MnO_2 (Sayilgan et al., 2009). Previous studies revealed that extraction mechanism of Zn was bio-acidic dissolution, and a combined action of bio-acidic dissolution of MnO and Fe^{2+} mediated reduction of MnO_2 was responsible for the release of Mn (Xin et al., 2012). Therefore, Zn extraction was a rather fast process, Zn almost reached the maximum extraction concentrations after only 1 day of contact under different pulp densities; whereas Mn dissolution was a relatively slow process, the maximum doses were attained after 13 days of culture (Xin et al., 2012). Furthermore, the maximum released doses of Zn increased from 2800 to 6700 mg/l with increase of pulp density from 1% to 8% (w/v); however, the extraction efficiencies decreased from 100% to 29.9% based on the

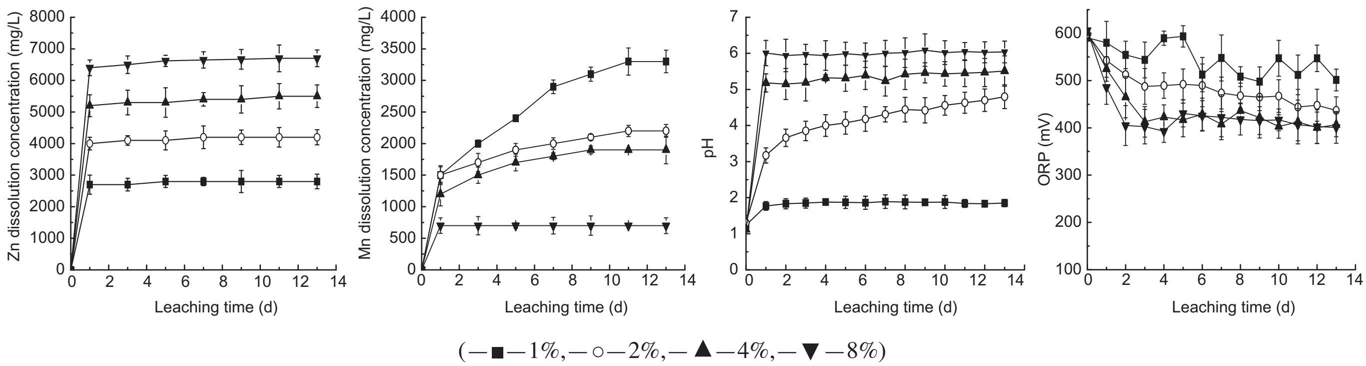

Fig. 1. Time-courses for Zn extraction dose, Mn extraction dose, pH value and ORP value during bioleaching of the spent Zn–Mn batteries under different pulp densities.

content of Zn in the batteries powder being 280 g/kg. In contrast, the maximum released doses of Mn decreased from 3300 mg/l at pulp density of 1% to 700 mg/l at 8%; especially the extraction efficiencies drastically decreased from 94% to only 2.5% based on the content of Zn in the batteries powder being 350 g/kg. The increase of pulp density displayed a great adverse effect on extraction of both Zn and Mn, especially the latter.

As described above, high pulp density in the batch culture allowed a great reduction in the volume of bioleaching media which resulted in low extraction cost of metals, and a huge increase in released concentration which was favorable to the subsequent recovery of metals from leaching media in the case of nonoccurrence of extraction efficiency decline. In the field of biohydrometallurgy, the pulp densities of ores were often 10% or higher (Rossi, 1990). However, with bioleaching of spent batteries the pulp densities were 1% or lower due to very high content of both metals and alkaline matter which were toxic to the bioleaching bacteria (Cerruti et al., 1998; Mishra et al., 2008a; Xin et al., 2009). Therefore, reasons analysis for the efficiency decline and countermeasures exploration for improving the bioleaching yields at higher pulp densities such as 2%, 4% and 8% were very important not only for the spent Zn–Mn batteries but also for other batteries types from both academic research and practical application.

With pulp density of 1%, the pH value of bioleaching media rose from 1.0 to 1.8 after 1 day of contact with the spent batteries due to release of the alkaline matter from the batteries (Fig.1); nevertheless, the pH value of 1.8 still allowed the growth and maintenance of activity of the both acidithiobacillus as the mixed culture. Therefore, despite the consumption of H_2SO_4 for extraction of Zn and Mn by acidic dissolution as well as for fight with the alkaline matter, the pH value kept almost unchanged at about 1.8 over the whole bioleaching period of 13 days due to continuous generation of H_2SO_4 from oxidization of sulfur by the sulfur-oxidizing bacteria (Xin et al., 2012). On the other hand, strong fluctuation of ORP in high level of 550 mV indicated high activity of the iron-oxidizing bacteria and occurrence of oxidization/reduction between Fe^{3+}/Fe^{2+} and Mn^{4+}/Mn^{2+} which was driven by the iron-oxidizing bacteria, resulting in transformation of insoluble MnO_2 into soluble MnO (Xin et al., 2012). As a result, the high activity of both acidithiobacillus assured efficient reduction of MnO_2 into MnO and complete acidic dissolution of both ZnO and MnO, witnessing 100% of Zn extraction and 94% of Mn release at 1% of pulp density (Xin et al., 2012).

When pulp density increased from 1% to 2%, 4% and 8%, the pH value of leaching media increased respectively from 1.8 to 4.8, 5.5 and 6.0 after 13 days of contact with the spent batteries due to growing amount of the released alkaline matter. The resulting pH value of 4.8 or higher displayed inhibiting effect on the activity and growth of both acidithiobacillus, especially the iron-oxidizing ones whose optimum pH for growth and activity were ca. 2.0. The high pulp density led to high pH value of bioleaching media, the high pH value resulted in low activity of the sulfur-oxidizing bacteria, the low activity of the bacteria determined the low leaching efficiency of Zn from 100% at pulp density of 1% to 29.9% at 8%, because the extraction of Zn was due to the acidic dissolution by biogenetic H_2SO_4 which was mainly driven by the sulfur-oxidizing bacteria. In contrast, Mn existed in the form of both soluble MnO and insoluble MnO_2. Since pH value of 4.8 or higher at pulp density of 2% or higher resulted in almost complete inactivation of the iron-oxidizing bacteria as was shown in ORP illustration of Fig.1 that the ORP value kept a very low level with almost no fluctuation at pulp density of 2% or higher, preventing MnO_2 into MnO by reduction action drove by the iron-oxidizing bacteria; the single acidic dissolution by the sulfur-oxidizing bacteria witnessed an evident decline of Mn extraction concentration from 3300 mg/l at pulp density of 1% to 700 mg/l at 8% and corresponding decrease of extraction efficiencies from 94% to only 2.5%.

3.2. Reasons analysis for decrease of bioleaching efficiency of Zn and Mn from spent batteries at high pulp densities

In general, the high toxicity from the high released doses of metals or the deteriorated environmental conditions such as pH or ORP which affected the growth and activity of leaching bacteria were often the underlying reasons for bioleaching efficiency decline at high pulp densities. However, in the present studies the mixed culture with both 10 g/l Zn^{2+} and 10 g/L Mn^{2+} displayed almost the same activity as the controls free of both Zn^{2+} and Mn^{2+}, which were shown by the pH value variation and ORP value change, indicating high resistance of the mixed culture on toxicity of both Zn^{2+} and Mn^{2+} (Fig.2). It was concluded that the decline of bioleaching efficiency of both Zn and Mn was not attributed to toxicity effect of the released metals.

By counting the cell number of the mixed culture over the bioleaching period, it was found that with 1% of pulp density the cell number was increased in the first 8 days, followed by a slight decline after 13 days of leaching; whereas the cell number sharply decreased in the process of bioleaching at pulp density of 8% and was about 4.7% of that at 1% of pulp density after 13 days of bioleaching (Fig.3). The results indicated that the deteriorated environmental conditions involving pH and ORP at high pulp densities caused decrease in cell number of the mixed culture, which was responsible for the leaching efficiency decline. The activity test of acidithiobacillus further demonstrated that the pulp density somewhat linearly damaged the activity of the sulfur-oxidizing bacteria; higher pulp density resulted in lower activity of the sulfur-oxidizing bacteria, generating less H_2SO_4 and higher final pH value (Fig.4). On the other hand, the iron-oxidizing bacteria of the mixed

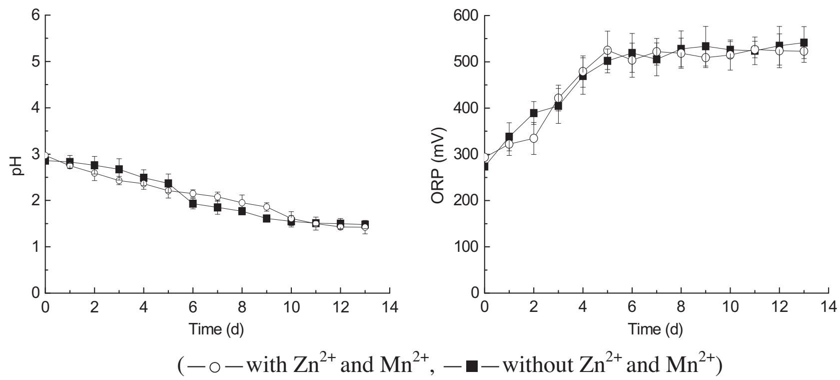

Fig. 2. Comparison of the change behaviors of both pH value and ORP value in the bioleaching media containing the mixed energy matters with or without both 10 g/L Zn^{2+} and 10 g/L Mn^{2+}.

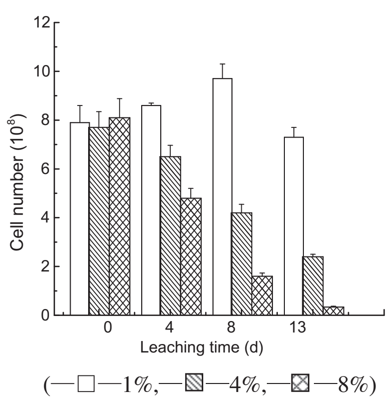

Fig. 3. Variation of the cell number of the mixed culture during bioleaching of the spent Zn–Mn batteries under different pulp densities from 1% to 8%.

culture was almost inactivated at 2% of pulp density or higher, as was shown by the almost unchanged ORP values using pyrite as energy substrate (Fig.4). It was the almost linear reduction of the activity of the sulfur-oxidizing bacteria with increase of pulp density that witnessed the declined bioleaching efficiency of Zn; it was the almost complete inactivation of the iron-oxidizing bacteria at 2% of pulp density or higher that witnessed the declined bioleaching doses of Mn.

3.3. Improving bioleaching performance of the spent batteries at pulp density of 4% by reducing the initial pH value of bioleaching media

The released concentrations of both Zn and Mn as well as the variation of both pH value and ORP value under different initial pH value as a function of bioleaching time at pulp density of 4% were illustrated in Fig. 5. The initial pH value had great effect on bioleaching efficiency of both Zn and Mn, and reducing initial pH value of the leaching media evidently enhanced extraction of both Zn and Mn. When the initial pH value decreased from 3.0 to 1.0, the final released dose of Zn increased from 1000 to 5500 mg/l, equivalent to from 8.9% to 49% in leaching yield; whilst the maximum dissolved concentration of Mn rose from almost 0 at pH 2.0 or higher to 1900 mg/l at pH 1.0 (Fig. 5), equivalent to from 0% to 13.6% in leaching yield. On the other hand, the pH value of the bioleaching media was kept about 5.0 over the whole period of leaching in the case of initial pH 1.0; whereas the pH value rose to above 6.4 at initial pH 2.0 or higher, resulting in greater inhibiting effect on activity and growth of the mixed culture, as shown in the very low ORP value of even below zero (Fig. 5). In a conclusion, increases of initial pH value deteriorated the environmental conditions and thus inhibited the activity of the bioleaching bacteria, leading to great decline in leaching yield of both Zn and Mn. Therefore, reducing initial pH value of leaching media was an efficient way to improve extraction performance of both Zn and Mn.

3.4. Improving bioleaching performance of the spent batteries at pulp density of 4% by increasing concentration of energy matters of bioleaching media

The released concentrations of both Zn and Mn as well as the variation of both pH value and ORP value under varied doses of energy matter as a function of bioleaching time at pulp density of 4% were illustrated in Fig. 6. It was obvious that increase of dose of energy matters improved considerately the bioleaching efficiency of both Zn and Mn, especially the latter. With increase of dose of the mixed energy substrates from 4 to 16 g/l, the extraction

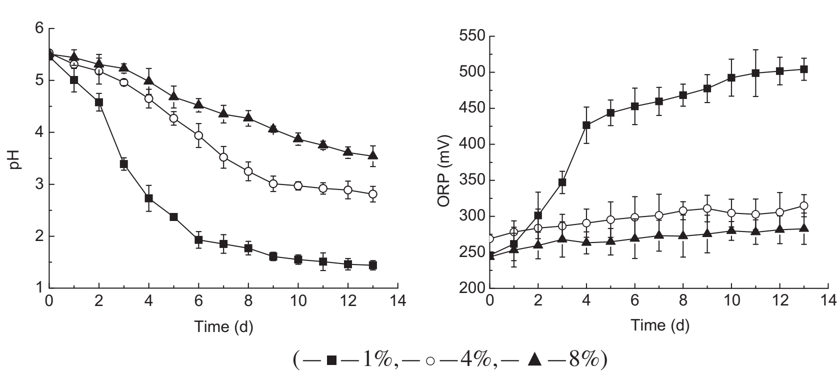

Fig. 4. Activity detection of the mixed culture from 13-day-old bioleaching systems with different pulp densities from 1% to 8% as a function of pH change using sulfur as the sole energy substrate or ORP change using pyrite as the sole energy substrate.

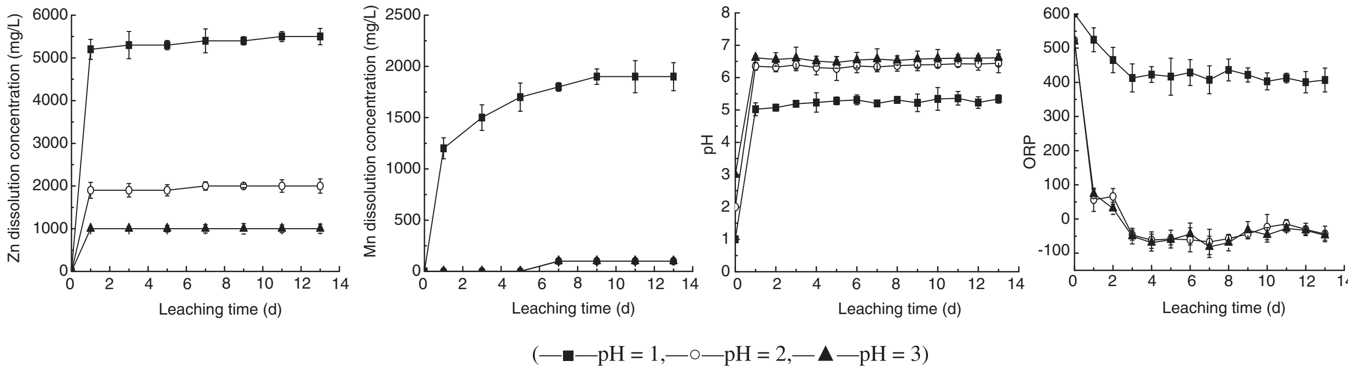

Fig. 5. Time-courses for Zn extraction dose, Mn extraction dose, pH value and ORP value during bioleaching of the spent Zn–Mn batteries under different initial pH value at pulp density of 4%.

concentration of Zn increased from 5500 to 8960 mg/l, equivalent to from 49% to 80% in bioleaching efficiency; meanwhile, the released dose of Mn drastically rose from 1900 to 9910 mg/l, equivalent to from only 13.6% to 71% in bioleaching efficiency. Based on pH change profile of bioleaching media, it was found that the pH value kept approximately 5.0 during bioleaching with 8 g/l of energy matters or lower; however, the pH value reduced to about 4.0 with 16 g/l of the mixed energy matters. It was mainly because that the increased dose of sulfur enhanced the production of biogenetic H_2SO_4 from oxidization of sulfur, resulting in lowest pH value which not only benefited to release of both Zn and Mn by acidic dissolution but also advantaged to activity and growth of the mixed culture. On the other hand, the lowest pH value and the increased dose of pyrite greatly promoted the generation of biogenetic Fe^{3+} which brought about more amount of Fe^{2+}. The strongest reduction of insoluble MnO_2 into soluble MnO by the more amount of Fe^{2+}, along with the strongest acid dissolution by the lowest pH at 16 g/l of the mixed energy matters was responsible for the huge increase in extraction efficiency of Mn by 5.2-fold from 13.6% to 71%.

3.5. Improving bioleaching performance of the spent batteries at pulp density of 4% by exogenous-acid adjustment of media during bioleaching

The released concentrations of both Zn and Mn as well as the variation of both pH value and ORP value as a function of bioleaching time at pulp density of 4% in the case of exogenous-acid adjustment or not during bioleaching were illustrated in Fig. S1 in the Supporting Information. It was clear that periodical exogenous-acid adjustment to pH 2.0 during bioleaching evidently promoted the extraction performance of both Zn and Mn. Compared with the case without adjustment, the exogenous-acid adjustment increased extraction dose from 8960 to 11160 mg/l for Zn and from 9910 to 12410 mg/l for Mn, attaining the maximum extraction efficiency of almost 100% for Zn and 89% for Mn. It was no doubt that periodical exogenous-acid adjustment improved environmental conditions of pH set at lower level and of ORP set at high level and thus enhanced the activity and growth of the mixed culture (Fig. S1), causing a rather great increase in leaching yield of both Zn and Mn. The results showed that periodical exogenous-acid adjustment of the bioleaching media was also an efficient way to improve leaching performance.

3.6. Bioleaching kinetics of Zn and Mn from the spent batteries at pulp density of 4% under the optimum conditions

The bioleaching kinetics of Zn and Mn from the spent batteries under the optimum conditions, i.e. the initial pH 1.0, the mixed energy substrates dose of 16 g/l and exogenous-acid adjustment during bioleaching, were investigated by establishing the mathematical relationship between the fraction of metal dissolved and the bioleaching time using various kinetic models according to Mishra et al. (2008b), including diffusion controlled model, chemical reaction controlled model, shrinking sphere model (Stokes regime) and product layer diffusion model. Equations for the lines of best fit were given in Table 1 for each model with the respective correlation coefficients. The results suggested that the chemical reaction controlled model fitted best for describing the Zn bioleaching behaviors. Since the progress of reaction would not be affected by the presence of any product layer, the quantity of batteries leaching was proportional to the available surface of unreacted core. As a result, the reacting particles got shrunk during the reaction and finally disappeared, attaining almost complete leaching of Zn (Mishra et al., 2008b). However, with Mn bioleaching behavior, the diffusion controlled reaction approached the linearity more closely than the others, meaning that the resistance to

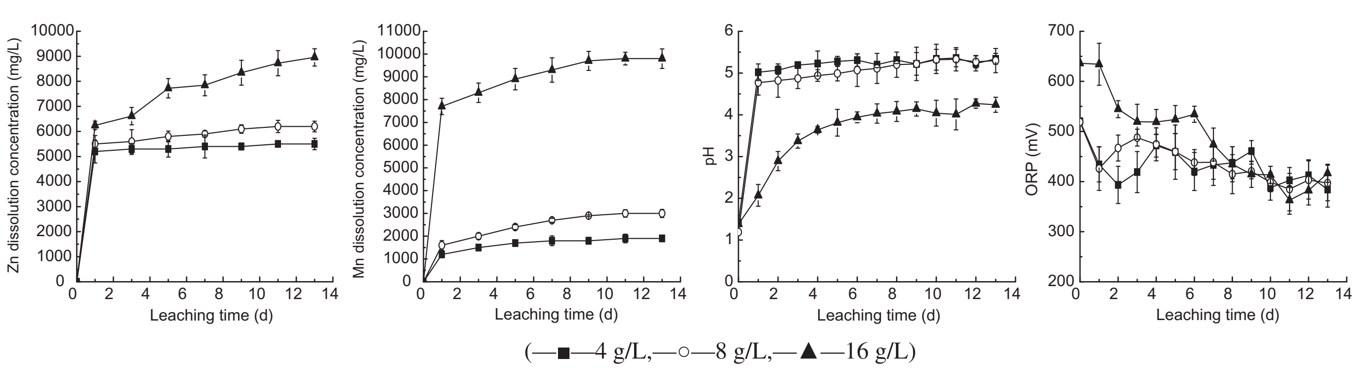

Fig. 6. Time-courses for Zn extraction dose, Mn extraction dose, pH value and ORP value during bioleaching of the spent Zn–Mn batteries under different concentrations of the mixed energy matters at pulp density of 4%.

Table 1
Lines of best-fit equations and correlation factors for various kinetic leaching models describing the extraction of Zn and Mn from the spent batteries at pulp density of 4% under initial pH value of 1.0 and 16 g/L of the mixed energy substrates with adjustment using exogenous acid during bioleaching.

Kinetic model	Line of best-fit and correlation factor	
	Zn	Mn
Chemical reaction controlled	$Y = 0.0526X + 0.2648$, $R^2 = 0.9839$	$Y = 0.0210X + 0.2628$, $R^2 = 0.9763$
Diffusion controlled	$Y = 0.0221X + 0.0662$, $R^2 = 0.9584$	$Y = 0.0099X + 0.0543$, $R^2 = 0.9846$
Shrinking sphere, Stoke's regime	$Y = 0.0396X + 0.5435$, $R^2 = 0.9138$	$Y = 0.0252X + 0.4676$, $R^2 = 0.9554$
Product layer diffusion, parabolic	$Y = 0.0451X + 0.5070$, $R^2 = 0.8482$	$Y = 0.0349X + 0.3748$, $R^2 = 0.9531$

diffusion through a product layer controlled the rate of reaction of the bioleaching of spent batteries (Mishra et al., 2008b).

3.7. Bioleaching mechanism exploration of the spent Zn–Mn batteries by EDS

The micro-area analysis for determining the content change of both Zn and Mn in the residues of the spent batteries during bioleaching was carried out using EDS (Fig. S2 in the Supporting Information). The results directly demonstrated that Zn was quickly extracted at day 1 of bioleaching, resulting in low ratio of Zn in weight compared with Mn (Fig. S2). After 13 days of bioleaching, Zn was completely extracted; whereas Mn was partially released as shown by a certain amount of Mn detected in the residues of the spent batteries (Fig. S2).

3.8. Bioleaching mechanism exploration of the spent Zn–Mn batteries by XRD

The residues of spent batteries after 13 days of bioleaching were analyzed using XRD for determining the existing form of Mn and compared with that of the raw samples (Fig. S3 in the Supporting Information). The results displayed that the remained Mn of about 11% in the spent batteries was existed in the form of MnO_2.

4. Conclusion

Extraction efficiencies of Zn decreased from 100% at 1% of pulp density to 29.9% at 8% of pulp density, with Mn from 94% to 2.5%. Both cell number reduction and activity decrease of the mixed culture at higher pulp densities caused worse bioleaching performance. Reducing initial pH value of leaching media, increasing concentration of energy matters and exogenous-acid adjustment of media during bioleaching witnessed the maximum extraction efficiency of 100% with Zn and 89% with Mn at 4% of pulp density. However, measures for improving bioleaching efficiency at pulp density of 8% or higher were needed to be further studied.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2012.02.133.

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